Compositional Redistribution During Casting of $Hg_{0.8}Cd_{0.2}Te$ Alloys

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Abstract

A series of $Hg_{0.8}Cd_{0.2}Te$ ingots were cast both vertically and horizontally under well-defined thermal conditions by using a two-zone furnace with isothermal heat-pipe liners. The main objective of the experiments were to establish correlations between casting parameters and compositional redistribution and to develop ground-based data for a proposed flight experiment of casting of $Hg_{1-x}Cd_xTe$ alloys under reduced gravity conditions. The compositional variations along the axial and radial directions were determined by precision density measurements, infrared transmission spectra, and x-ray energy dispersion spectrometry. Comparison between the experimental results and a numerical simulation of the solidification process of $Hg_{0.8}Cd_{0.2}Te$ is described.

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Introduction

One of the major bulk growth techniques for $Hg_{1-x}Cd_xTe$ is the solid state recrystallization or quench-anneal method (1). In this technique, a melt is cast to form a polycrystalline solid ingot, which is then annealed at a temperature just below the solidus temperature so that the ingot can rapidly recrystallize. During the casting process, compositional inhomogeneities in the solid are inevitable mainly because the first to freeze segment will have higher mole fraction, x, of CdTe, than the last to freeze portion. This is a direct result of the wide separation between the liquidus and solidus of the HgTe-CdTe pseudobinary phase diagram (2). Compositional variations can also be caused by diffusion, convection, and Stokes migration (buoyant rising or settling) of solid particulates. Experimentation under reduced gravity in space is expected to minimize buoyancy-related solute redistribution effects and expected to result in more homogeneous castings. In this paper, we present the experimental results of the compositional redistribution during the casting of $Hg_{0.8}Cd_{0.2}Te$ melts. These will serve as part of the ground-based data for a proposed space flight experiment.

A series of $Hg_{0.8}Cd_{0.2}Te$ ingots were cast with both horizontal and vertical orientations relative to the gravity vector under well-defined thermal conditions provided by a two-zone furnace equipped with heat-pipe isothermal liners. The axial and radial compositional variations were determined by precision density measurements, Fourier Transform Infrared (FTIR)

transmission-edge mapping, and Energy Dispersive X-ray (EDX) analysis. A comparison between the experimental data and the results from a one-dimensional numerical simulation of the rapid solidification process of $Hg_{1-x}Cd_xTe$ alloys by Alexiades et al. (3) is also described.

Experimental

The starting materials were six 9 grade Cd and Te from Cominco American, and triple distilled instrument Hg from Bethlehem Apparatus. The ampoules were made from T08 commercial grade 16 mm OD, 3 mm wall-thickness fused silica tubing supplied by Heraeus Amersil. The elements were weighed out for x = 0.20 samples with some extra Hg added to compensate for the high Hg pressure over the melts. The ampoules were sealed under vacuum after the elements were loaded. Adhesion of HgCdTe samples to silica ampoule walls, or "wetting," during the homogenization process was eliminated by using the procedure described previously (4). A two-zone furnace system with heat-pipe liners was used to cast the ingots. The furnace system set-up has been described in detail in Ref. 5. A typical temperature profile used is shown in Fig. 1. The ampoule was first located at an initial position with a surrounding temperature of 820±3 °C. The casting process was accomplished by moving the furnace by about 35 cm such that the ampoule reached its casting position with a surrounding temperature of 652±5 °C. The movement of the furnace was completed in less than 10 s. The lengths of the vertically cast ingots were about 9 cm. The length of a horizontally cast

ingots was, typically, 15 cm with 50 to 60% of the circular cross section filled. The two-zone furnace with heat-pipe liners provided well-defined thermal boundary conditions required for the theoretical simulation of the solidification process. Table 1 lists the casting conditions for seven x = 0.2 ingots including four vertical and three horizontal ones.

Characterizations and Results

Microstructure

Selected slices were cut perpendicularly to the long axis of each of the ingots. The ingots showed various degrees of recrystallization. The grain sizes varied from about 20 grains in the 1 cm diameter cross section for C2-B (annealed at 650 °C for 1 hr.) to about 10 grains for C2-D and F (at 650 °C for 7 hrs.). Second phase inclusions with diameter of, typically, 40-70 μm were found in all the slices. The EDX spectra showed that these precipitates were essentially pure Te. The density of these Te-inclusions ranged from 600 to 1500 cm^{-2} for the vertically cast ingots. However, in the semi-circular cross sections of the horizontally cast ingots, C2-G and H, there were almost no Te inclusions observed in the top surface layer of about 1 mm thickness. The Te-inclusion density for the remaining bottom portion was about 300 cm^{-2}.

Precision Density Measurements

The average compositions of selected slices were determined by precision mass density measurements. The technique was

described in details elsewhere (6). Figure 2 shows the axial compositional distributions for two vertically cast ingots, C2-D and C2-F. Similar results for a horizontally cast ingot, C2-H, are shown in Fig. 3. The thicknesses of the slices were between 1.5 and 2.0 mm.

Infrared Transmission-Edge Measurements

The radial compositional distribution in each slice was determined from the absorption edge of the IR transmission spectrum. The transmittence was usually below 1% for a 1 mm thick slice cut from a vertically as-cast ingot. Presumably, the low transmission was due to free carrier absorption associated with large hole concentration in the ingots. Usually the transmittence improved to 5-15% after the slice has been annealed at 300 °C for 5 to 7 days in equilibrium with a Hg reservior at 290 °C. However, 0.7-mm thick planks that were cut along the flat upper surface of the horizontally cast ingots showed about 5% transmittence even before annealing. Each of the vertically cast ingot showed large compositional fluctuations along the radial directions. No clear pattern of the compositional distribution, e.g., Cd-rich or Hg-rich in the center, was observed. Figure 4 shows a typical compositional profile along the diameter of a slice. The aperture used for the transmission measurements was 100 μm. For the horizontally cast ingots, the compositional variations were rather small in the directions perpendicular to the gravitational acceleration, especially in the area near the free surface. Figure 5 shows the x-variations

in a rectangular section cut horizontally from the top flat surface of C2-G ingot. The average composition ($\bar{x}$) is 0.209 with a standard deviation, s = 0.0031. For the slices cut from the long-annealed (at 650 °C for 457 hrs.) horizontally cast ingot C2-I, the compositional variations in its semi-circular cross section show a definite pattern. As shown in Fig. 6, the mole fraction of CdTe in the upper portion of the slice is larger than the lower portion and the composition along the horizontal directions is quite uniform. For instance, the average composition $\bar{x}$ for the o-s is 0.2064 with a standard deviation of $s = 5.8(10^{-4})$ and $\bar{x}$ for the x-s is 0.2035 with $s = 8.2(10^{-4})$. The slices cut from other two horizontally cast ingots, C2-G and C2-H, show similar behavior although not as pronounced as for C2-I.

EDX Analysis

An electron microprobe analysis technique using energy dispersive spectrometry has been developed in this laboratory (7) for quantitative analysis of $Hg_{1-x}Cd_xTe$ at a spatial resolution of 5 μm. Figure 7 shows the results from EDX measurements along the radius of the C2-C-3.45 cm slice. The data shows fluctuations in x similar to the IR transmission results shown in Fig. 4. The solid line corresponds to theoretical values calculated from a detailed one-dimensional model developed to predict compositional redistribution during rapid solidification of HgCdTe and similar semiconducting alloys under diffusion limited conditions [3]. The model deals mathematically with the

wide separation between the solidus and liquidus of the $Hg_{1-x}Cd_xTe$ pseudobinary phase diagram [2] as well as with the variations in the pertinent alloys thermophysical properties with temperature and composition. A numerical solution to the model predicts a 0.1 mm thick Cd-rich surface layer. Figure 8 shows a blown-up plot of the experimental data in the surface region and in agreement with the calculations indicates a 0.1 to 0.15 mm thick Cd-rich layer.

Discussions

Each of the three characterization techniques used here has its own advantages and they complement one another as well. Mass density measurements give the average composition of each slice and thereby yield a measure of the compositional variations along the ingot axis. IR transmission technique is a fast and convenient method to map out the compositional variations within a slice. EDX analysis gives the high resolution needed to profile fine-scale spacial variations. In Figs. 2 and 3, comparisons between the results of density measurements and the compositions obtained by taking the average of the IR transmission results over the whole slices are shown. Apparently the consistency between the density measurements and IR transmission mapping is reasonably good.

The fact that the upper surface regions of the horizontally cast ingots are free of Te inclusions and show significant IR transmission even before Hg annealing is believed to be due to the in-diffusion of Hg atoms contained in the free volume. This

result is in agreement with previous work (8,9) that indicated that the in-diffusing Hg can annihilate Te-precipitates and reduce the metal vacancy concentration (which acts as doubly ionized acceptor) in the skin region during a low temperature Hg-saturated annealing.

Both the axial and radial compositonal profiles show considerable amount of fluctuations, approximately ±0.08, as seen in Figs. 2 to 4. It should be pointed out that if there are any voids or microcracks inside a slice, the density measurements will give an average x-value that is larger than the actual. This is probably the reason why the overall composition of C2-F, shown in Fig. 2, is somewhat larger than 0.20.

The rapid solidification process employed during casting readily lead to homogeneous nucleation of solid-phase particles, richer in Cd (higher x) than the melt, from the constitutionally supercooled HgCdTe liquids. In turn, these particles, as well as the dendrites that are broken off from the solidification interface, are expected to float upwards because their densities are less than those of the melts. This phenomenon of buoyant rising of solid particles, or Stokes migration, was seen during a vertical Bridgman-Stockbarger type crystal growth of the alloys [10]. For growth rates greater than those permitted by the constitutional supercooling criteria ($g/R \gtrsim 1.5 \times 10^6$ K.s/cm^2, where g is the temprature gradient in the melt and R is the solidification rate) [6], the top portion of the crystals were rich in CdTe. The axial compositional data for a vertically cast ingot shown in Fig. 2 shows no clear evidence for this effect.

Apparently, in this case, the particle migration velocities were significantly smaller than the solidification rates.

Although the casting conditions differed somewhat from the boundary conditions used in the calculations, the thickness of the Cd-rich boundary layers were in good general agreement with those predicted by a one-dimensional diffusion model of Alexiades et al. [3]. In their calculations, a $Hg_{0.8}Cd_{0.2}Te$ cylindrical ingot of radius 0.6 cm, initially at temperature of 800 °C was exposed to an external temperature of 27 °C at time zero. The calculations predicted that at 15.6 s the surface started to solidify at the composition x = 0.277. The ingot was completely solidified at 140.6 s with x = 0.195 at the center while the surface composition fell slightly to 0.274 due to the non-zero solid diffusivity. The solid line in Fig. 7 shows the compositional profile at this time which is essentially the steady-state composition except for the continuing drop at the surface. For instance, the surface composition fell to 0.256 at 1000 s and 0.250 at 1500 s.

Finally, as indicated by the data in Fig. 5, the horizontal casting procedure used yielded materials with reasonably uniform compositions along the axial direction which were void of Te-inclusions.

Acknowledgements

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References

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Figure Captions

Fig. 1 Temperature profile for the casting experiments. The ampoule was initially at "initial position" and reached "casting position" by moving the furnace. The relative directions of gravitational acceleration are also shown for both vertical and horizontal castings.

Fig. 2 Compositional variations along the axial direction for vertically cast samples determined by mass density measurements. The circles are for ingot C2-F and the triangles are for C2-D. X at the distance of 3.3 cm for C2-D was the result obtained by averaging the IR transmission results over the whole slice.

Fig. 3 Compositional variation for horizontally cast sample C2-H. The circles are the results of density measurements and the triangle is the result of IR transmission measurements.

Fig. 4 Compositional profile along the radial direction of the vertically cast slice C2-C-6.77 cm by IR transmission measurements.

Fig. 5 Compositions measured by IR transmission in a rectangular slab cut horizontally from the top flat surface of the horizontally cast ingot C2-G between 7.0 and 7.9 cm. The average composition is $\bar{x} = 0.209$ with a standard deviaton of $s = 0.0031$.

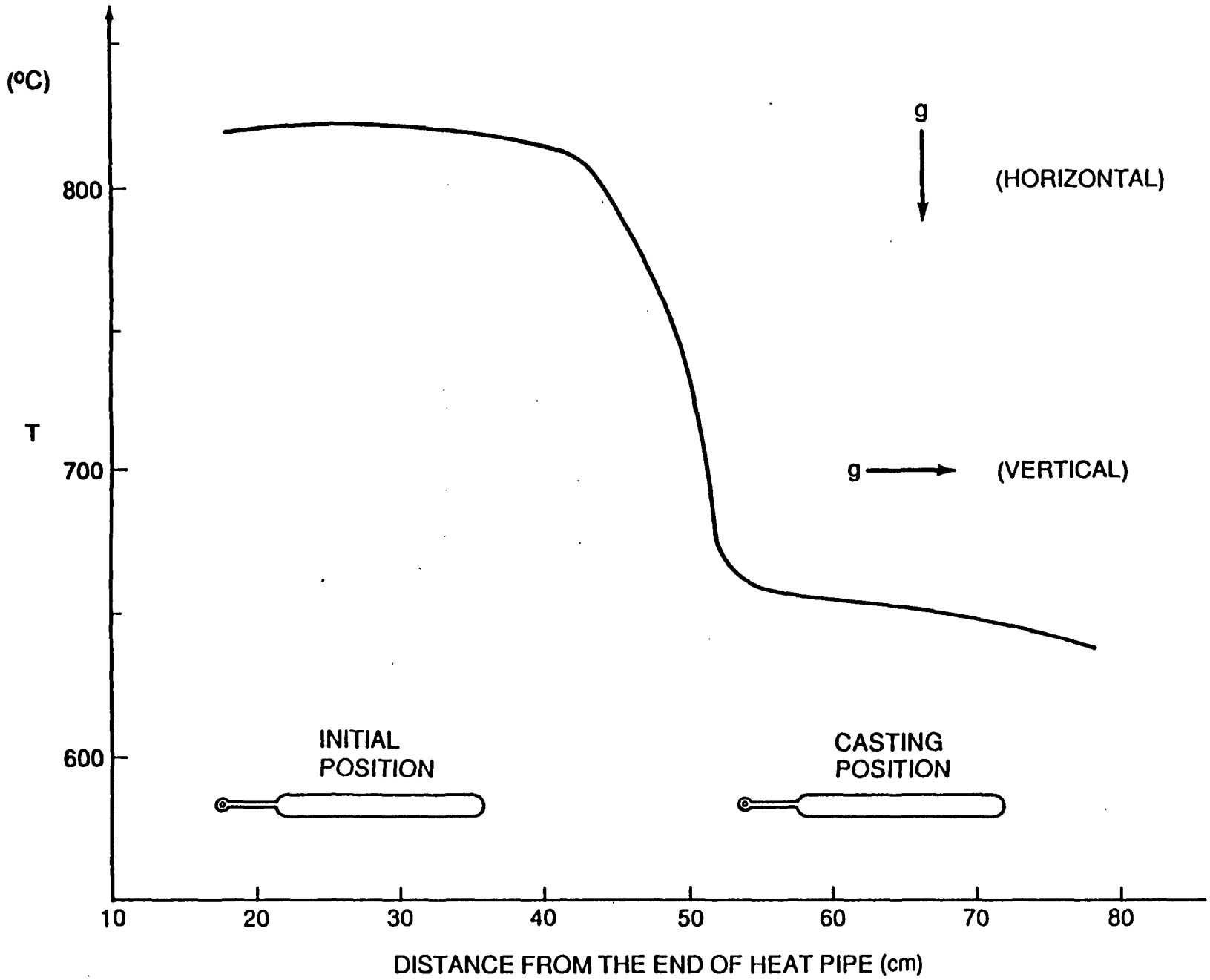
Fig. 6 Compositional profiles along the horizontal directions of the horizontally cast slice C2-I-3.05 cm by IR transmission measurements. The circles are the compositions along the line parallel to and at a distance of 1 mm from the flat surface. The x's are at 1 mm from the circles and the triangles are at 1 mm from the x's.

Fig. 7 Compositional profile along one radius of the C2-C-3.45 cm slice. The circles are the results of EDX analyses. A distance of 5 mm corresponds to the surface of the ingot and 0 mm corresponds to the center of the ingot. The solid curve is the calculated result from Ref. 3.

Fig. 8 A close-up plot of the experimental data of EDX near the surface region of the C2-3-3.45 cm slice.

Table 1. Casting Conditions for $Hg_{0.8}Cd_{0.2}Te$ Ingots

Sample	Time at 820 °C (hrs.)	Time at 650 °C (hrs.)	Vertical (V) or Horizontal (H)
C2-B	3	1	V
C2-C	19	2	V
C2-D	88	7.5	V
C2-F	41	7	V
C2-G	40	7	H
C2-H	56	7	H
C2-I	36	457	H


(°C)
800
T
700
600
g
(HORIZONTAL)
g
(VERTICAL)
INITIAL
POSITION
CASTING
POSITION
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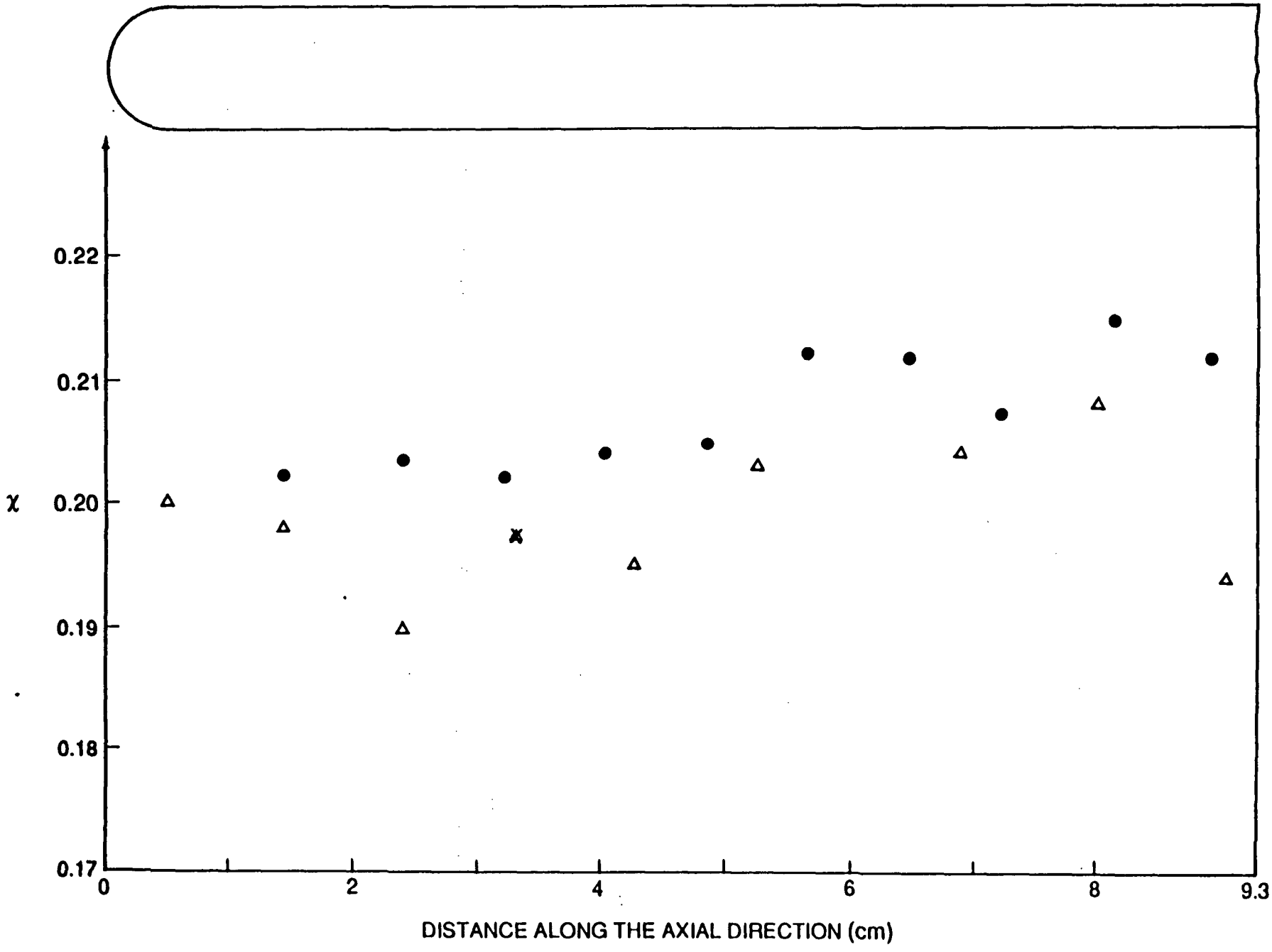
20
30
40
50
60
70
80
DISTANCE FROM THE END OF HEAT PIPE (cm)

Fig. 1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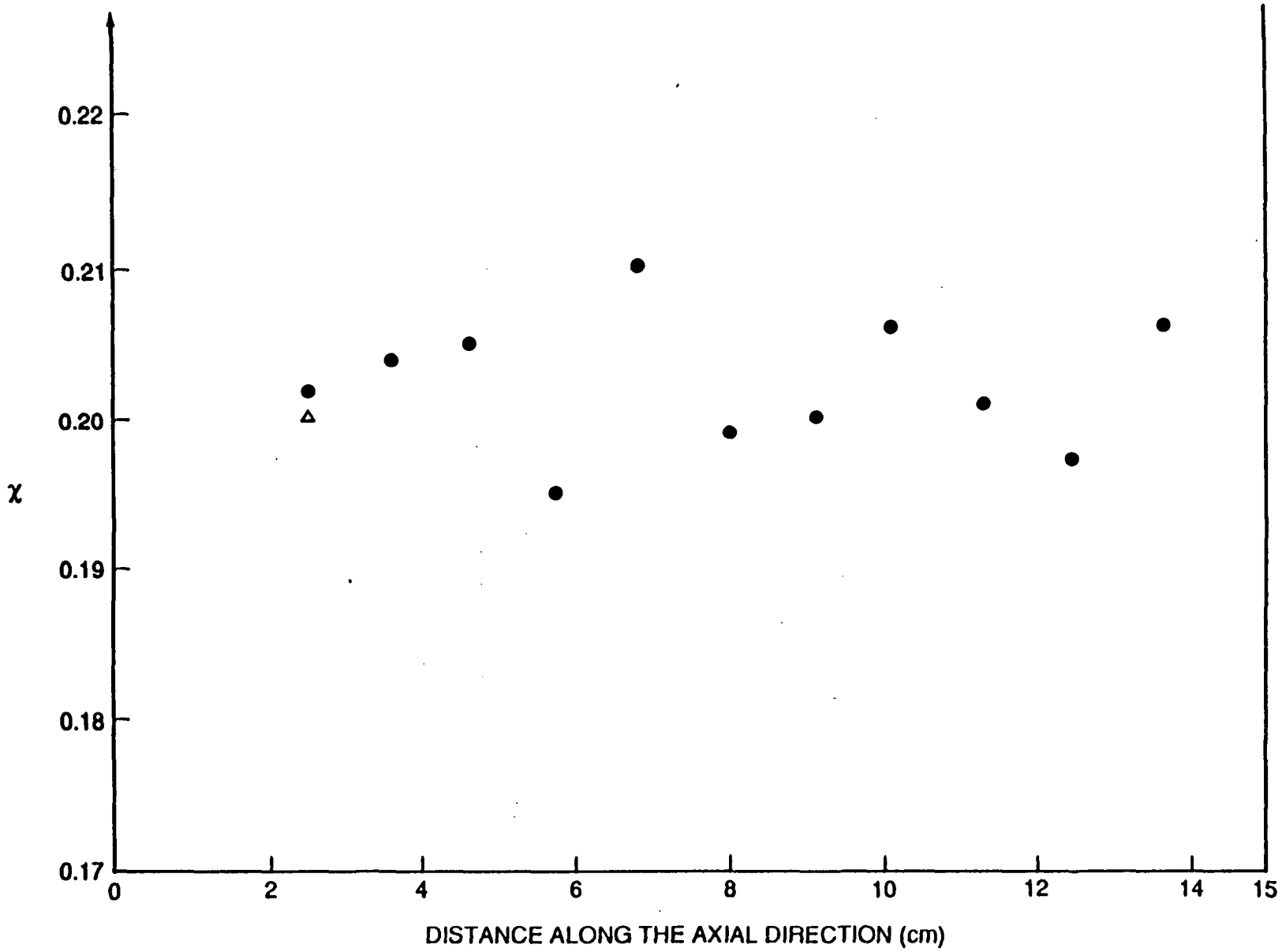
9.3
DISTANCE ALONG THE AXIAL DIRECTION (cm)

Fig. 2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0.19
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14
15
DISTANCE ALONG THE AXIAL DIRECTION (cm)

Fig. 3

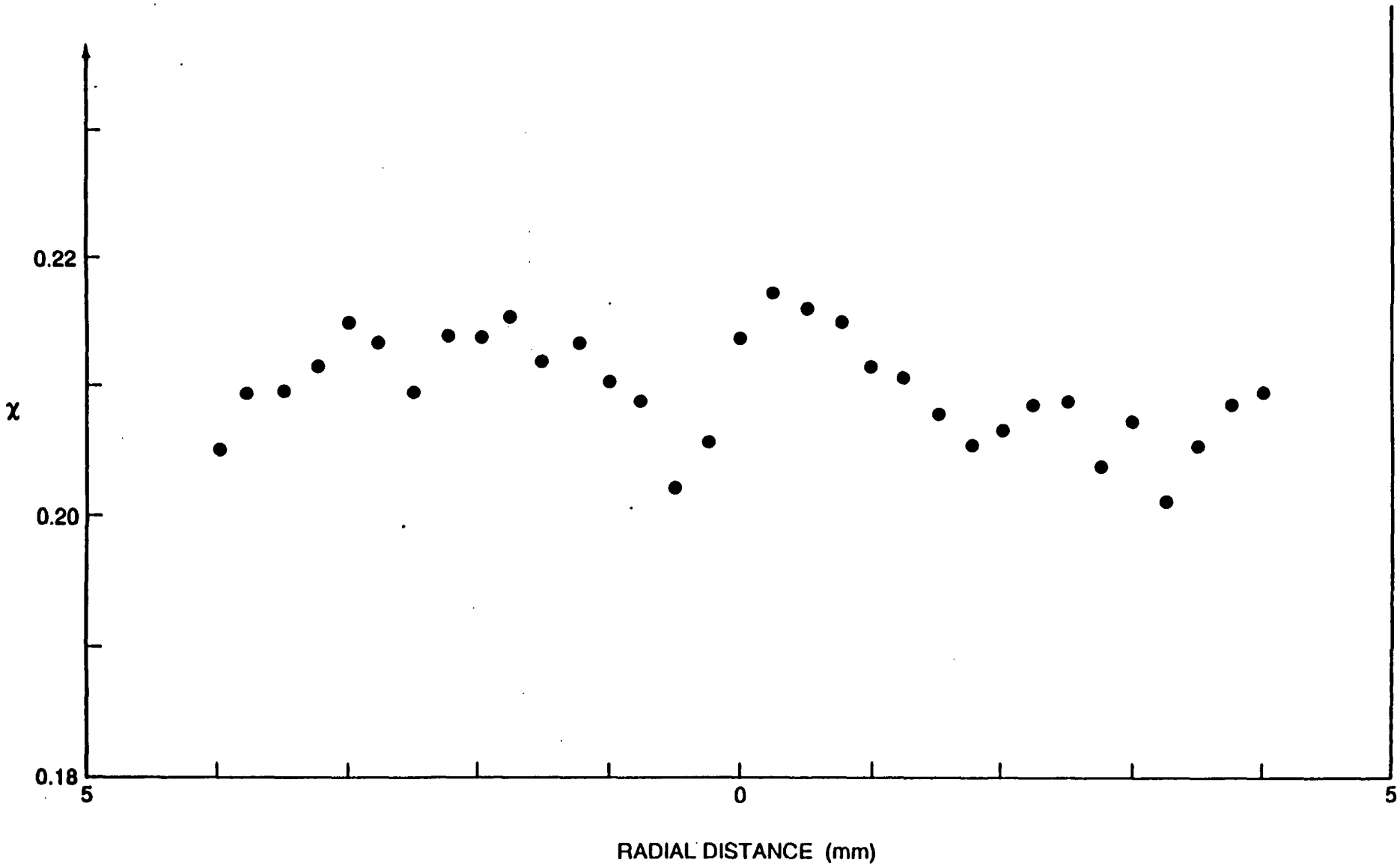
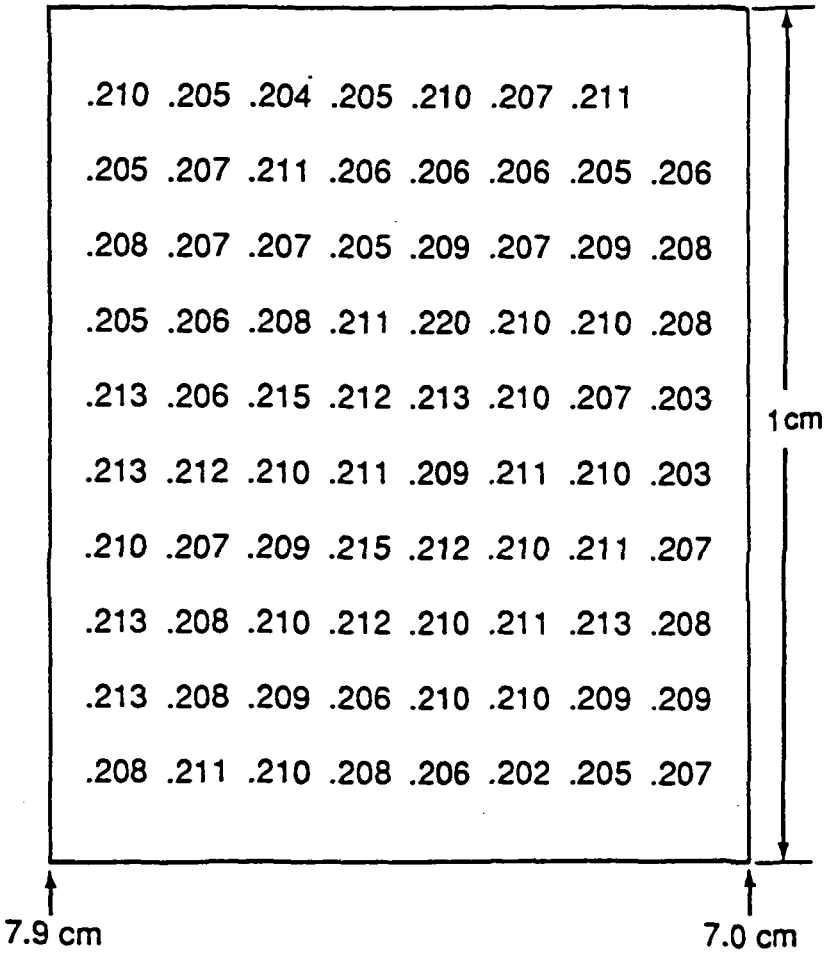


Fig. 4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.213 .208 .210 .212 .210 .211 .213 .208
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1 cm
7.9 cm
7.0 cm

Fig. 5

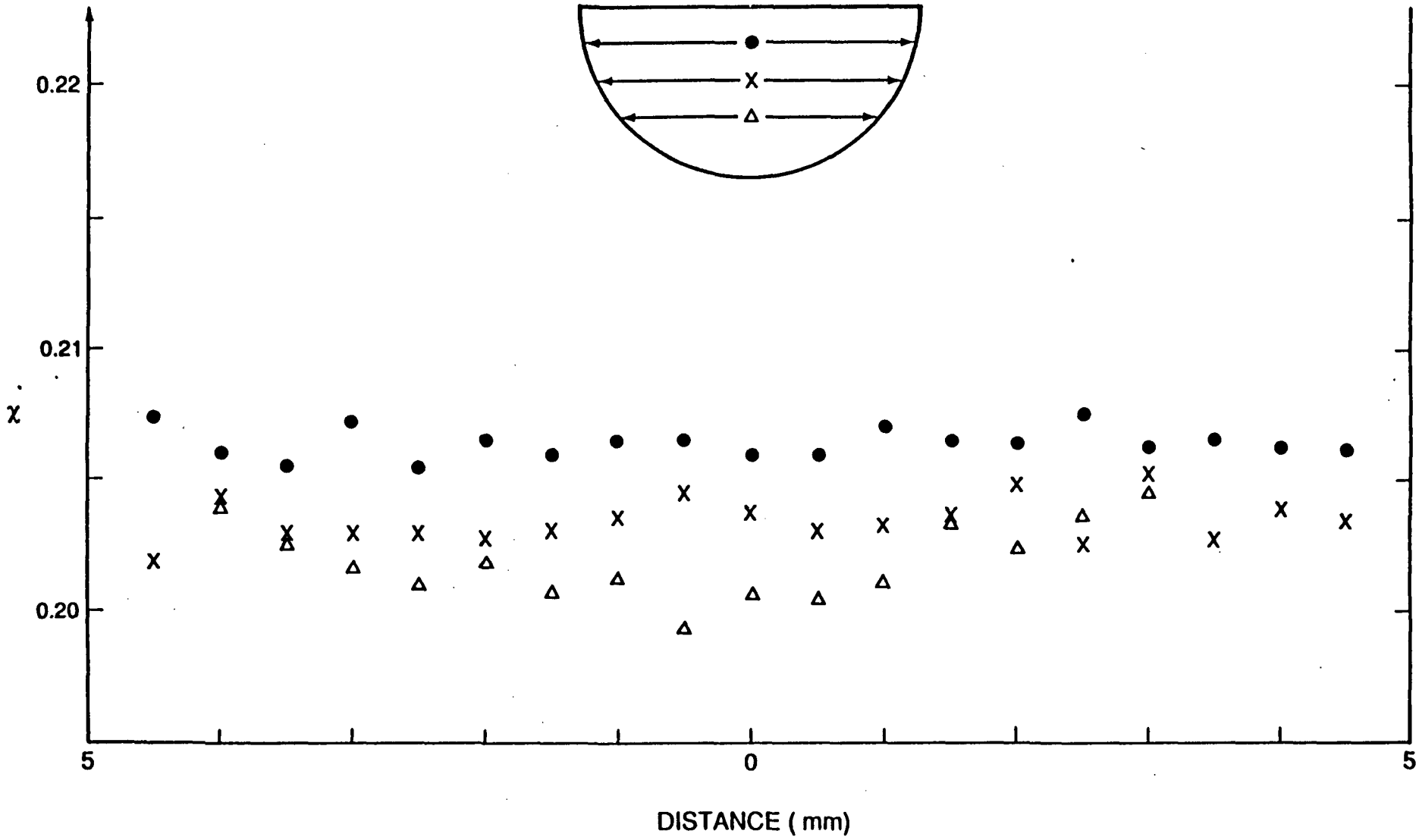
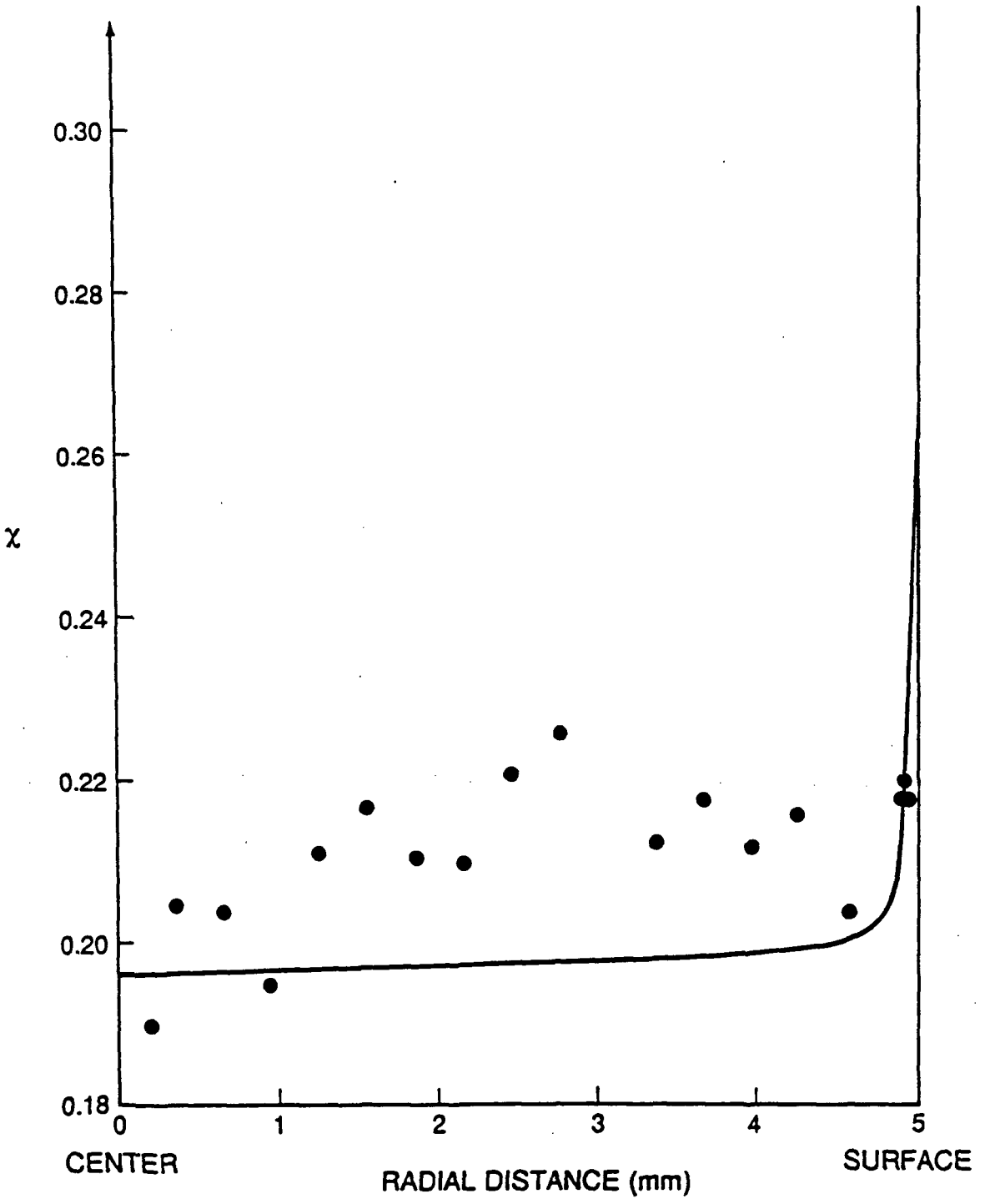


Fig. 6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0.28
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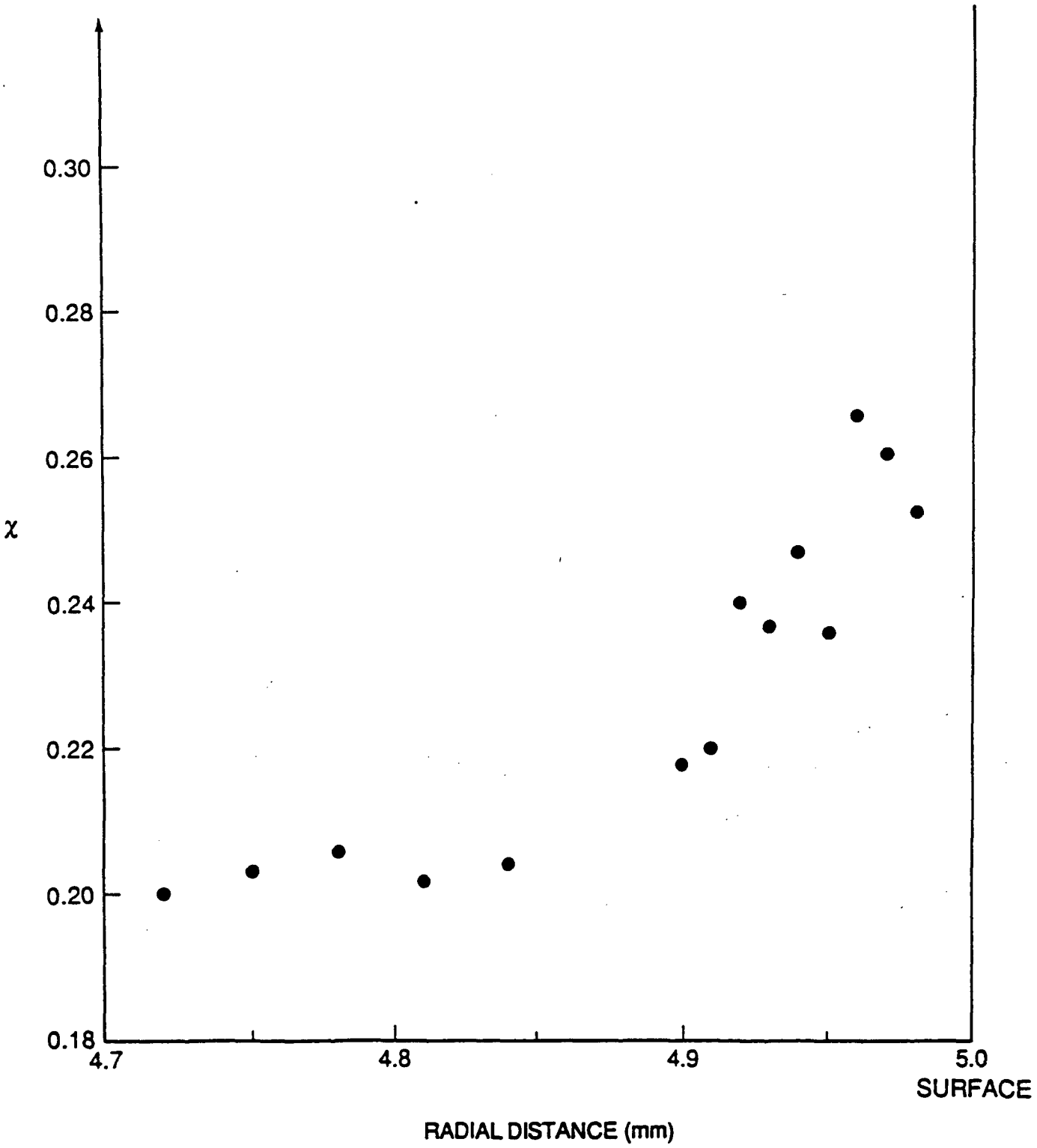
CENTER
RADIAL DISTANCE (mm)
SURFACE

Fig. 7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0.18
4.7
4.8
4.9
5.0
SURFACE
RADIAL DISTANCE (mm)

Fig. 8